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ADVANCES IN TECHNIQUES FOR STRUCTURAL AND DYNAMICAL STUDIES
OF STABILITY IN ENERGETIC MATERIALS
AND APPLICATIONS TO DIVERSE END-ITEM PROBLEMS

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A. INTRODUCTION

At recent Army Science Conferences, authors of the present paper have reported results of a continuing program aimed at the elucidation of the molecular dynamics and crystal structures of energetic materials and their relationship to stability (1-3). The systematic approach adopted represented not only a significant advance in our understanding of the dependence of macroscopic behavior on the microscopic properties of these materials, but also a considerable contribution to the understanding of the molecular properties of all complex substances.

The principal motivation for this program lies in the fact that although energetic materials technology has advanced considerably in the last several decades, a predictive capability concerning the response of a specific material to a variety of stimuli has still not been achieved. The present inability to make such predictions represents one of the fundamental limitations to the advance of energetic materials science and technology.

Recent theoretical results - both in a "conventional" analytical formalism (4,5), and using the relatively new technique of "computer molecular dynamics" (6) - suggest that, given certain experimental data, the sought-after predictive capability may be nearing partial realization. A portion of the present paper is devoted to the experimental advances that have been made in our program which will provide the needed data, i.e. the pressure and temperature dependences of interatomic forces in energetic materials.

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This effort represents one of several significant experimental advances in the state-of-the-art of solid-state science made, within our program, to elucidate the fundamental properties of energetic materials. An expected by-product of these advances is an increased capability to address specific applications problems by sophisticated techniques which are not routinely available. In the case of structural and lattice-dynamical probes this is illustrated in the present work by detailing the application of Raman spectroscopic and neutron scattering techniques to the solution of two diverse problems: 1) The non-destructive determination of grain orientation in shaped-charge liners; and 2) The determination of the low-temperature physical stability of ammonium nitrate/potassium nitrate ingredients in explosive fills.

→ This paper, then, consists of two distinct but closely related parts. In the first part we describe the most recent experimental advances that have been made in obtaining a predictive capability for the macroscopic behavior of energetic materials from structural and lattice-dynamical measurements. In the second part we describe two cases wherein sophisticated capabilities, developed previously, are being employed to aid in the solution of current development problems in energetic materials applications. ←

B. ADVANCES IN THE CORRELATION OF DYNAMICAL BEHAVIOR AND METASTABILITY

1. Background

"Lattice dynamics" is the term generally applied to the quantitative description of atomic and molecular motions in crystals and the forces of interaction which produce the motion. The theoretical and experimental techniques by which lattice-dynamical properties are determined have been described previously (1-3). The principal aspects to be considered here are that for a crystal of N particles, there are $3N$ vibrations, the spatial character and vibrational frequencies of which reflect the nature of the interatomic and intermolecular forces. Essentially, in an energetic material it is the response of the forces or bonds to different stimuli which produce the behavior of interest. (The response is also dependent on the presence of point defects, impurities, and extended defects such as surfaces. On the microscopic scale, they affect the environment and bonding of metastable molecular groups, and are therefore included, in principal, in the present discussion.) Characterization of the interatomic bonds is equivalent to an integration over specific electronic interactions. An approach in which the starting point is the electronic wave functions of the constituent atoms is also being pursued in our laboratory.

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The lattice dynamics of a simple solid (KBr) are shown in Figure 1 for three different directions in the crystal at two different pressures. The intermolecular vibrational states group themselves, when plotted as a function of the inverse wavelength ($1/\lambda \equiv q$) of the vibration, into "dispersion" curves each of which corresponds to a particular set of atomic motions. If the solid also contained molecular groups, additional higher energy dispersion curves would occur. These intramolecular modes would arise from atoms within a molecule vibrating against one another in different ways. Interatomic forces are inferred by assuming a set of forces, calculating the vibrational state spectrum, then adjusting forces until agreement between measurement and calculation is obtained. However, the measurement of vibrational state spectra is difficult, but possible by an approach which employs Raman, infra-red and neutron spectroscopic techniques. The use of all techniques is essential since each experimental probe samples only a portion of the complete vibrational state spectrum.

The past several years have seen increasing sophistication in the employment of the appropriate experimental techniques for the determination of the interatomic forces in energetic materials (1-3). However, theoretical developments have not been directed toward the correlation of lattice-dynamical measurements and chemical metastability until very recently, as described in the next section.

2. New Theoretical Approaches

The most promising new theoretical approach is that of "computer molecular dynamics" (CMD). In CMD calculations the position, velocity and acceleration of individual atoms, moving under realistic, anharmonic forces, are tracked as a function of time for a sample system (100-1000 atoms). This technique, then, offers the prospect of providing information on critical microscopic processes in energetic materials not obtainable in any other way (6). For example, the dependence of initiation on the power density and character of the initiating stimulus, the details of the different character of detonation observed in homogeneous and heterogeneous detonation, the directional character of decomposition in crystals have not been dealt with successfully employing conventional theory. Although employed to simulate the dynamics of simple systems for some years, new results for more complex systems such as liquid water, solid nitrogen, and model ferroelectric crystals are now being obtained. This technique has also been used (7) to test rate laws for very simple reactive systems and to describe the details of shock wave and heat pulse propagation in non-reacting solids (with rather surprising results). The thrust of these efforts is certainly in the direction of the description of the detailed time-dependent phenomena in realistic, reacting materials. A pre-requisite, however, is that

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FIGURE 1: Vibrational energy vs. inverse wavelength for three directions in KBr. Points and dashed lines: 6.2 kbar, Xs and solid lines 1 bar. Lines are the result of theoretical calculations.

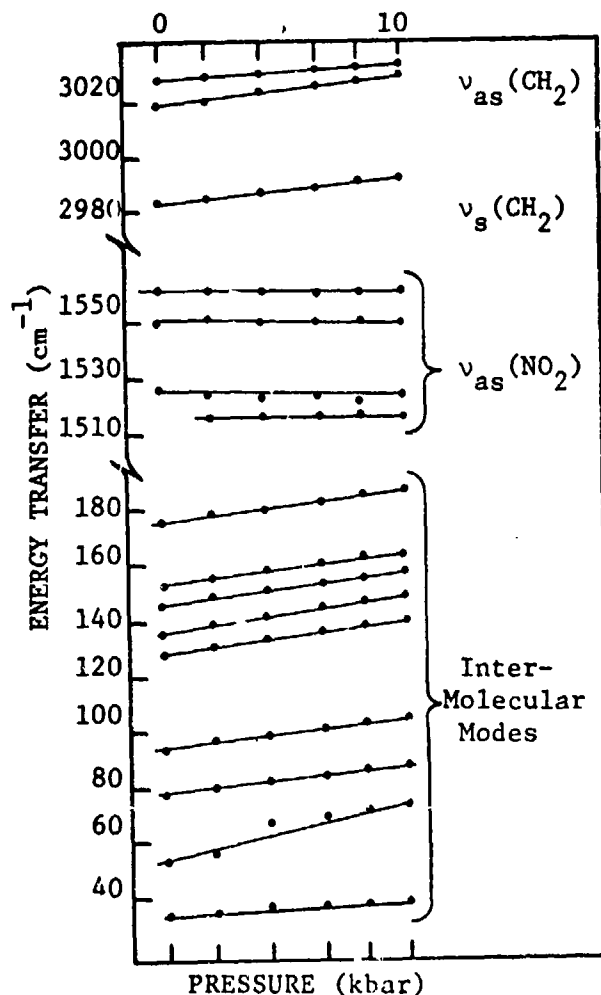
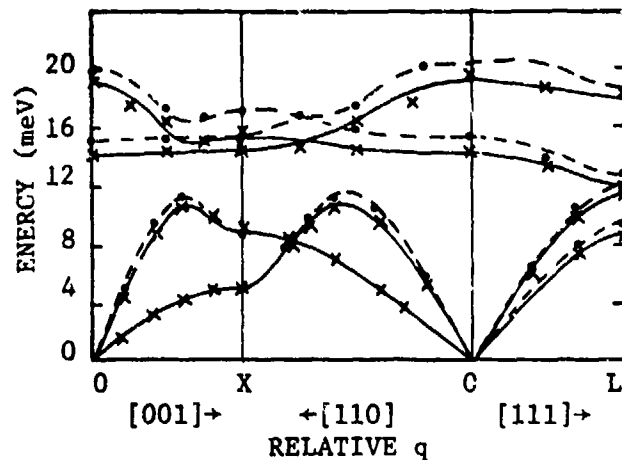


FIGURE 2: Pressure dependence of Raman-active modes in β -HMX. s and as denote symmetric and anti-symmetric intra-molecular stretching modes, respectively. Inter-molecular mode identification has been made (ref. 8) but has been omitted for convenience. (NOTE: $8.065 \text{ cm}^{-1} = 1 \text{ meV}$)

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accurate interatomic potentials obtained from pressure and temperature dependent lattice-dynamical measurements and details of chemical reactions be available.

Within this framework, very recent results obtained by conventional analytical techniques are of considerable interest. Pastine, Kamlet and Jacobs (4) have constructed molecular models to describe qualitatively the pressure and temperature dependence of mono- (or intra-) molecular decomposition and bi- (or inter-) molecular reactions in explosives. A few of the interesting results that come out of their model are: 1) that reaction rates are volume dependent, that a simple Arrhenius rate law may describe detonation processes only very crudely, and that activation energies determined under ambient conditions probably have little bearing on detonation processes; 2) that different rate processes are associated with different vibrational modes in certain types of decomposition, that intramolecular vibrational modes in which the frequency decreases with decreasing volume are expected to be associated with bond breaking, and that in the absence of such a mode there should occur a region of shock pressures in which monomolecular decomposition processes - dependent on increasingly large amplitudes of vibration - are forbidden; and 3) that spectroscopic measurements performed under high pressure are essential to clarifying the nature of monomolecular and bimolecular decomposition processes in general, and, in particular, to fully test their model.

The theoretical results of Pastine et al. are of considerable importance in themselves and as a means for facilitating the more powerful CMD approach. The next section describes the experimental advances that we have made to provide the essential information for a comprehensive description of critical microscopic processes in energetic materials.

3. New Experimental Capabilities

The theoretical developments described in the previous sub-section have provided added impetus to our on-going program already aimed toward increasing the temperature and pressure range over which structural and dynamical properties of energetic materials are measured (1-3). As mentioned earlier, to fully characterize dynamics, infra-red, Raman and neutron scattering are employed. Of these, neutron scattering is the most powerful in that it can sample the full range of $q (=1/\lambda)$ -space whereas Raman and infra-red are essentially restricted to $q \sim 0$ (see Figure 1). On the other hand, neutron scattering is, in general, less useful for the internal mode spectral region.

Neutron scattering studies of solids under pressure have been virtually non-existent, although pressure studies of most properties of solids have been reported for some time. We have made

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use of existing technology to construct a relatively simple pressure system useful to ≤ 12 kbar (8 kbar as presently configured) for neutron studies. Initial measurements to test the system were made on a very well-studied alkali halide, KBr (a simpler analog of potassium azide), and about which several somewhat conflicting theoretical descriptions have been developed.

The first complete measurement of the pressure dependence of dispersion curves of KBr is shown in Figure 1 for three crystallographic directions. The solid and dashed lines represent the results of our calculations of the lattice dynamics from assumed interatomic interactions at each pressure. The main point to be emphasized is that the measured pressure dependence of the higher energy (optical) modes is much different than that predicted by any semi-empirical calculation based on all previously available data including infra-red and Raman. This again shows the need for all available techniques for elucidation of the properties of energetic materials.

More immediately related to the Pastine et al. theory (4) are recent results obtained with a hydrostatic pressure system for Raman measurements (0-10 kbar). Data for some of the Raman active vibrational modes are shown in Figure 2 for β -HMX. Mode assignments are based on an extensive study of β -HMX and its isotope-substituted isomers at atmospheric pressure (8). Although limited in pressure range, it is clear that most of the modes increase in frequency in the expected way as pressure increases. However, the four anti-symmetric stretching modes of the NO_2 groups ($\nu_{\text{as}}(\text{NO}_2)$ schematically: $\text{O} - \text{N} = \text{O}$) exhibit a slight downward shift in frequency with increasing pressure suggesting increasing probability of dissociation. This is a very promising and reasonable result in that the nitro groups are those expected to be least stable, chemically. Furthermore, the absence of intermolecular modes having decreasing frequency with increasing pressure indicates that there should occur for β -HMX a pressure region in which bimolecular decomposition is suppressed down to some critical volume (4). Below this volume, the rate constant for bimolecular decomposition increases very rapidly.

The above qualitative discussion, though tentative in view of the limited data and limited pressure regime examined, suggests considerable complexity in the decomposition processes of β -HMX and is probably true in general. This possibility is neglected in conventional detonation calculations.

In addition to the neutron scattering pressure system now available for supporting studies, a diamond-anvil type pressure cell - useful for Raman and infra-red measurements - is also nearing completion. With this new cell, vibrational mode behavior can be examined to ≥ 200 kbar in a static environment. These combined capabilities should allow us to fully test the Pastine et al. theory

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and provide essential information for CMD calculations in the very near future.

C. UTILIZATION OF TECHNIQUES FOR SPECIFIC, APPLIED PROBLEMS

1. Background

In the previous section we have described state-of-the-art advances in the correlation of vibrational properties and fundamental energetic behavior. Although applications of the newly developed (pressure) techniques to other, more immediate, problems of DOD are not in progress at this time, previous experimental advances made within this program have subsequently been utilized to aid in the solution of problems in unexpected areas. Two examples of these types of applications are described in the following sub-sections.

2. Spin Compensation of Shaped Charge Liners

The optimum functioning of shaped-charge ammunition requires that the projectile have essentially zero spin (i.e. axial rotation) at impact with the target. This requirement cannot be achieved in practice; however, "overdesign" of the system can be used to achieve the desired penetration in spite of the degradation of the shaped-charge effect due to spin. On the other hand, optimum functioning can be achieved in spite of spin if the liner cone is manufactured in such a way that the individual grains (or crystallites) of the liner are aligned such that, as the liner collapses along preferred slippage directions, a counter-rotation equal to that of the in-flight projectile is imparted to the explosive blast jet. The achievement of the proper grain orientation to balance missile rotation is called "spin compensation" and it is used in several shaped charge munitions, among them the HEAT-T round which we will consider here.*

During manufacture, the same spin compensation must be achieved in all shaped charge liners or cones. To date the only method which was useful for determining the grain orientation in the manufactured copper cones has been x-ray diffraction. The procedure is straightforward: Bragg scattering from a crystallographic plane of copper is examined at a point on the cone for the largest possible range of orientations of the cone (α , 8 of Fig. 3 varied); if the grains are oriented, intensity as a function of cone orientation changes. In the case of copper liners examination of scattering from the slip planes (111) and planes in the slip direction (220) establishes the degree of grain orientation in the directions of

*It has also been suggested, but is currently believed to be less likely, that residual strains in the cone rather than grain orientation produce spin compensation. This possibility can also be tested by the technique which will be described.

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importance. The difficulty with x-ray diffraction, however, lies in the fact that for x-rays in the appropriate energy range (5-30 keV) the penetration is extremely small. Because of absorption alone, fewer than one in 10^4 of the incident x-rays (e.g. $\lambda = 1.54 \text{ \AA}$, $E = 8 \text{ keV}$) that penetrate to a depth of .01 cm re-emerge to be counted in a (standard) reflection measurement for copper. This limitation necessitates that examination of grain orientation within the bulk of the cone (thickness $\sim 0.28 \text{ cm}$) be preceded by destructive machining (and etching), followed by x-ray examination.

Current acceptance and quality control procedures in the case of the HEAT-T round are cumbersome and involve the following steps:

- 1) Delivery by a prospective manufacturer of a test batch of 50 cones, approximately two-thirds of which are test fired for different spin rates to test performance;
- 2) If performance is satisfactory the remainder are machined and etched to the believed critical depth and examined in a limited way (β and ϕ varied) by x-rays and grain orientation criteria established;*
- 3) Manufacturer spot checks cones in the course of production to assure that grain orientation falls within x-ray criteria;
- 4) Upon completion of a production batch of cones (~ 5000), army quality assurance examines with x-rays some twenty-five randomly selected cones and accepts or rejects the production batch;
- 5) Test firing of some twenty-five additional cones to determine performance is done for information purposes after acceptance.

If variations in performance and grain orientations were small, the procedure outlined above would be satisfactory; however, this is not generally the case. In fact diffraction averages from consecutive cones of the same lot may vary 50% or more of the established allowable range so that one must question the validity of correlating the x-ray examination of unfired cones with the performance of fired cones from the same batch (see also next subsection). Furthermore the critical depth at which orientation should be examined is based on unconfirmed theoretical calculations. The problems outlined above were described as long ago as 1967 (10); however, no alternative technique has been proposed to alleviate the situation which came to the attention of the authors of the present paper relatively recently. It appeared that neutron diffraction, with which considerable work had

*An x-ray examination technique has been developed in which the full range of orientations is examined (2). This procedure is not yet used in cone procurement.

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been done in studying the structures of energetic materials (1-3 and references cited therein), offered decided advantages over x-rays in certain aspects of the problem.

Neutron and x-ray diffraction are essentially identical except that neutrons scatter from nuclei and x-rays from electrons. The difference in interactions, however, leads to a much greater penetrating power for neutrons for virtually all materials. In contrast to x-rays, only 10% of incident (1.08 Å) neutrons would be lost by absorption in transiting two cone thicknesses (0.56 cm copper). This immediately suggests the possibility of determining grain orientations in intact cones, nondestructively, followed by firing of examined cones to establish grain orientation/performance criteria with certainty. Progress to date is described in three sub-sections below.

a. Comparison with x-rays.

The first measurements with neutrons were on a piece (2.5 x 2.5 cm) cut from a liner, flattened, machined and etched for x-ray examination. Diffraction intensities for all orientations of α and β (Figure 3) can be plotted in a so-called "pole figure" diagram for each crystal plane examined. Such a diagram is shown in Figure 4 for the (220) planes of copper as obtained with neutrons. The results show that the neutron examination is quite comparable in sensitivity (or contrast between oriented and unoriented regions) to the x-ray technique (9). The presence of high (and low) intensity regions is indicative of regions of preferential grain orientation in the liner; however, the symmetric distribution of these regions about the center of the figure corresponds to no overall preferred orientation and essentially zero spin compensation for this sample.

b. The effect of annealing.

After fabricating a fixture to examine grain orientation in intact HEAT-T liners it was clear that part of the "distortion" of the diffraction patterns arising from the conical shape of the liner could be corrected for if a cone with no oriented regions were also examined. Earlier, Schiff and Donadio (11) attempted to use annealing to reduce the spin compensation of over-compensated cones. They used a partial x-ray scan (θ and ϕ varied) to determine the time vs temperature change of diffraction intensity for a batch of cones of a "single" spin compensation. From this they inferred the appropriate anneal time for cones fabricated with another spin compensation, and fired "annealed" and un-annealed cones to ascertain the change in performance. Their conclusion was that their choice of anneal time/temperature had reduced spin compensation too much.

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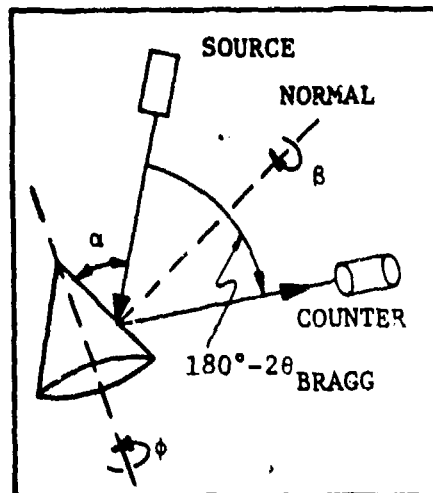


FIGURE 3: Schematic of scattering geometry for grain orientation determination in shaped charge liners for neutrons or X-rays.

FIGURE 4: "Pole figure" for piece cut from HEAT-T liner, obtained with neutrons. Relative intensities of various regions are 0-3, 4-7, 8-11, ≥ 12 (solid black).

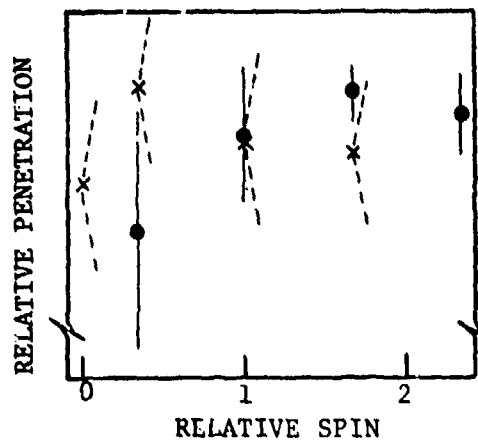
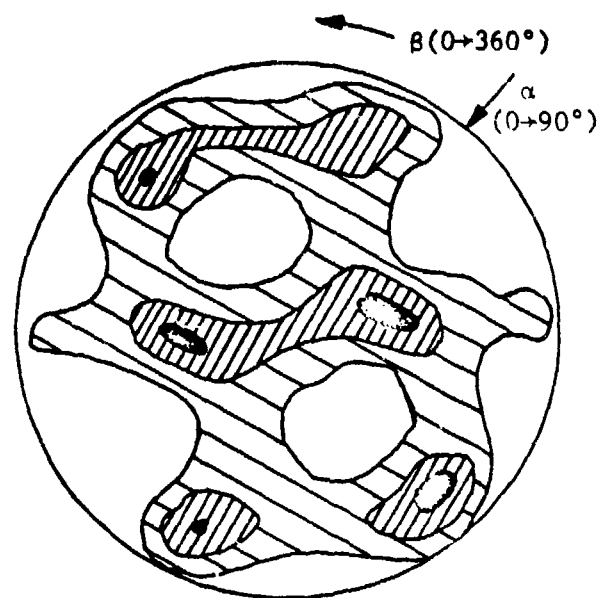


FIGURE 5: The performance vs. spin results of ref. 11 with appropriate standard deviations. Points with solid lines correspond to un-annealed liners, Xs with dashed lines to annealed liners. (Note: exact values are classified.)

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We have examined a single cone with neutrons "as received" and after annealing at a temperature/time for which "complete" annealing (11) should occur. Neutron diffraction of this cone after annealing shows that although grain orientation has changed, considerable preferred orientation remains. This led us to re-examine the results of Schiff and Donadio, plotted in Figure 5 with appropriate standard deviations (NOTE: exact values are classified). There is a suggestion that the standard and annealed round penetrations show maxima at spins of 1.67 and 0.33, respectively. However, one could equally well draw straight lines of zero slope through each set of data points. This is not at all surprising when one considers that for twenty cones (from the same batch that the cones for the performance data of Figure 5 were obtained) the average x-ray diffraction reading - indicative of spin compensation - was 319 with a standard deviation of 202.* With so large a standard deviation it is clear that one could partially anneal a standard round and still have a spin compensation considerably greater than one of the un-annealed standard rounds. This again shows the importance of characterizing and performance-testing the exact same rounds.

c. Neutron examination and performance testing

A program has been established in which cones, non-destructively examined with neutrons - will be introduced into the post-acceptance firing program for cones now being produced. To date (111) and (220) pole figures, using 1 A wavelength neutrons, have been measured for twelve cones fabricated at the same time. The pole figure patterns of the twelve are very similar (but not identical) which suggests that the current manufacturer is maintaining good short-term quality control. Before firing, (111) and (220) pole figures will be obtained for the same cones using a different neutron wavelength ($\lambda = 2.4$ A). A comparison of pole figures obtained at the two wavelengths will provide some measure of the difference in grain orientation as a function of depth in the cone, and the true critical depth - if such exists - for performance. Formulation of a computer code by which pole figure measurements can be analyzed to extract quantitative estimates of spin compensation is in progress. Finally, before firing, additional cones from the same manufacturer will be obtained and examined to establish long-term quality control.

*It is unfortunate that Schiff and Donadio chose the batch of cones that they did for the most important study. A batch used for another study gave x-ray readings of 203 ± 30 for 28 cones. Nevertheless, even if this latter batch were performance tested, the criticism made above would be valid.

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In summary, with this new approach to establishing spin compensation/performance correlations for shaped charge liners, we feel that some of the long-standing questions in this area will be answered very soon.

3. Low Temperature Stability of AMATEX-20K

Ammonium nitrate (AN) is an energetic material with enormous potential importance for military use. However, its use has been curtailed, in part, because of the presence of at least five polymorphic forms at atmospheric pressure as illustrated in the phase diagram (12) of Figure 6. In particular, in pure AN the IV \leftrightarrow III transition (at $32.3^{\circ}\text{C} = 90^{\circ}\text{F}$), which occurs with normal amounts of water present, is accompanied by a large change in volume. Thermal cycling through the phase transition is accompanied by irreversible expansion, extrusion of charge and malfunctioning of munitions.

The addition of potassium nitrate (KN) to AN has been proposed as a means of changing the phase diagram so that the IV \leftrightarrow III transition would no longer be a problem. Indeed, Figure 6 indicates that at a concentration of 10 wt. % KN, the phase transition is suppressed to near 0°C . Although 0°C is certainly a temperature through which thermal cycling would still be expected, the phase diagram determination (x-ray diffraction of very wet samples) showed (12) the transition from phase III to be relatively sluggish, and the phase transformed to be phase IV or V (III \leftrightarrow V is not accompanied by a large volume change). The kinetics of the transformation and the exact identification of the resultant phase (with realistically dry samples) remained undetermined.

Laser Raman scattering, with a few confirmatory measurements using neutron diffraction, has proved to be a highly selective and convenient means to provide the needed information. Identification of phases was possible in a straightforward manner by inspection of the ν_1 band of the NO_3 internal mode spectrum, as shown in Figure 7. Studies were conducted on neat AN/KN prills. Concurrently, the effects of cold temperature regimes on cased and uncased charges were determined. The Raman studies showed that the phase changes occur more sluggishly than in AN, and that moisture strongly influences the time of phase change and the sequence. With low moisture content (≤ 0.2 wt %) transiting the phase change temperature in the direction of temperature decrease causes a III \rightarrow V shift to occur. A higher moisture content results in a combination of III, IV and V phases in the prill. Upon warming, the phase change sequence is always V \rightarrow IV \rightarrow III. The times to first phase change for a temperature decrease mode are: for a moisture content 21%, ~ 3 hrs, for moisture contents between .05% and 1%, 1-5 days, increasing to ~ 2 weeks for samples that were purposely dried to extremely low moisture content. Upon continued cycling the time required for the phase change

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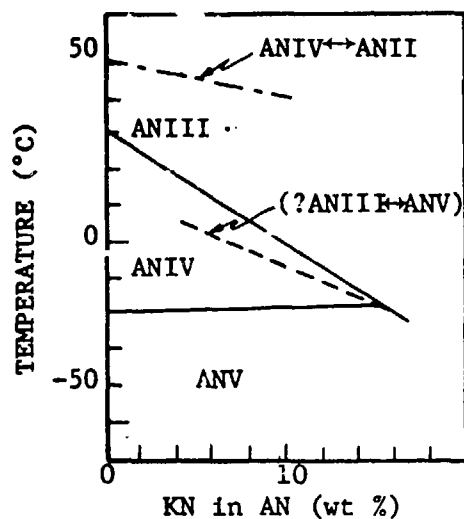


FIGURE 6: Partial phase diagram of KN in AN (ref. 12). The upper dashed line denotes the absence of phase III at low water contents. The lower dashed line denotes a not well established phase line.

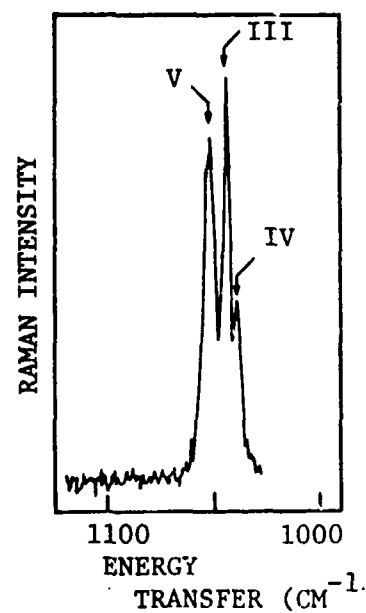


FIGURE 7: The NO_3 ν_1 internal mode region for 10%KN in AN showing the presence of phases III, IV and V.

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to occur diminishes rapidly. If the results of cast moisture analyses were juxtaposed to the results of this study it would be seen that in the cast, the first III \rightarrow V phase shift would occur after approximately 3 days storage at temperatures below the phase change temperature.

The result of these studies clearly shows that the use of 10% KN/90% AN prills does eliminate the high (90°F) temperature cycling problem; however, low temperature dimensional stability would remain a difficulty. On the other hand, preliminary low temperature stability measurements on 20% KN/80% AN show no indication of a phase transition even after 25 days of cold storage. We conclude that some concentration between 10 and 20% KN in AN may well yield both acceptable dimensional stability and explosive performance; further laboratory study is in progress.

D. SUMMARY AND CONCLUSIONS

In the present paper, a diversity of research efforts have been described. In each case the techniques and expertise employed are the outgrowth of a continuing program in a complex and difficult technical area: the quantitative understanding of the fundamental microscopic properties and identification of critical parameters in energetic materials.

In this area, we have developed new capabilities for the measurement of structural and dynamical properties at high pressure. Because of recent theoretical advances, our increased experimental capabilities are timely and essential. We can now provide data both for testing the new theoretical models and for extending to complex materials sophisticated calculations which have the potential for describing transient phenomena at the atomic level - a regime not previously explored.

We have also given two examples of how techniques previously developed for the study of fundamental properties of energetic materials are now being used to examine immediate problems of an applied nature. The advantage of a broad capability is illustrated by the number of techniques by which the problems could be successfully examined. In the case of the low temperature stability of AN/KN solid solutions, a variety of available probes could have been employed to obtain the desired information: x-ray diffraction, neutron diffraction, Raman scattering. Two of these were in fact used with the large fraction of information coming from Raman spectroscopic studies. In contrast, it appears that the only technique by which the grain orientation of shaped charge liners can be determined non-destructively is by neutron diffraction. The use of this technique to establish the true spin-compensation/performance

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correlation coupled with subsequent (destructive) x-ray diffraction examination for production quality control suggests itself.

In summary, the present work shows that a true predictive capability for energetic materials behavior is nearing realization. Furthermore, the experimental techniques which have been developed to provide this capability are yielding important data on applied problems in unanticipated areas. We expect that existing capabilities, and techniques which are currently being developed, will play a similar two-fold role in the future.

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